学 位 論 文 内 容 の 要 旨

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学 位 論 文 題 名

Controlled Synthesis of Nanoparticles and Composites via Sputtering in Liquid
(液中へのスパッタリングによるナノ粒子とそのコンポジットの制御された合成)

Nature challenges scientists, and many secrets for its perfection in creating macrostructures lie in the nanoscale regime. This study aims at improving the understanding of the behavior of nanoparticles and nanoclusters synthesized using a sputtering into liquid. This synthesis method is important in terms of simplicity of the process and high purity of the samples: nanoparticles and nanoclusters are generated in the vacuum, without using reducing agent and toxic solvents. The design of their characteristics, composition and size, can then be controlled by using appropriate sputtering conditions and by choosing the sputtering media wisely. The dissertation presents and discusses the use of the above mentioned synthesis method for the production of nanoparticles-polymer hybrid materials. The study on the chemicophysical stability/transformation and optical properties of the nanoparticles was performed, as understanding about stability and nanoparticle behavior in a determinate ambient conditions is of fundamental importance for future applications and safety.

Titanium dioxide, TiO_2, nanoparticles (NPs) are important wide-bandgap materials used as UV-active photo-catalysts and various optical applications such as a UV block material in sunscreens, or to increase the refractive index of thin films and polymers. Besides, stoichiometric titanium monoxide, TiO, with narrow bandgap and strong visible-light absorption can be used for energy harvesting or catalyst applications towards the visible region. Therefore, the preparation of titanium oxides with control of its oxidation state offers a facile way to modify the optical properties of hybrid materials that contain titanium oxide NPs. It is still a challenge to use chemical methods for synthesizing clean titanium oxides of very small size (1–10 nm) with controlled composition dispersed in polymers since the decomposition of titanium complexes can result in various undesired titanium oxide phases and re-dispersion of pre-made NPs can cause agglomeration. My study proposed sputtering of Ti in liquid under controlled atmospheric conditions (oxygen content) for the direct synthesis of different titanium oxides embedded in liquid monomer and resin. Pentaerythritol ethoxylate (PEEL) with low vapor pressure was chosen as liquid substrate to obtain uniform dispersions of titanium oxide NPs. Titanium oxide (TiO_x, x = 1, 2) NPs with diameters of 4 nm with a controlled composition by adjusting the sputtering atmosphere were successfully prepared. Furthermore, as the electronic structure of the TiO_x NPs can change depending on the particle size, crystallinity and degree of oxidation, we were able to modify the optical properties of PEEL and the resin by embedding TiO_x NPs in the matrix. The enhancement of the refractive index with high transparency and low dispersion of a resin containing TiO_2 NPs was observed. In addition, PEEL and resin containing TiO NPs were produced with strong visible absorption. This synthetic approach was demonstrated promising for the advanced preparation of highly pure TiO_x NPs for various applications in optical devices, energy conversion, and light harvesting in the UV-visible region.

Inorganic fluorescent probes and inorganic fluorescent-polymer hybrid composites are in the centre of much attention over the past few years. Many methods to stabilize metallic nanoclusters have been developed, trying to obtain highly versatile optical properties. Metallic nanoparticles, when in small enough in size, start showing discrete energy levels, and size-dependent properties, giving them a great advantages in terms of versatility. Gold and silver nanoclusters have been widely studied due to their non-toxic, higher stability and high photoluminescence emission extinction. In this study we describe the synthesis of, cheaper and more abundant, copper metallic photoluminescent nanoclusters using the sputtering method into a polyethylene glycol 600 (PEG) and mercaptoundecanoic acid (MUA), as well into pentaerythritol tetrakis(3-mercaptopropionate) (PEMP). The liquid media were chosen for their different amount of thiol moieties to cap the copper nanoclusters. We obtained stable nanoparticles with a size of 1.6 ± 0.2 nm in case of PEG-MUA mixture, showing luminescence emission at 440 nm. In case of sputtering into the thiol rich liquid (PEMP), a different behavior appears: at first the product shows similar photoluminescence properties with an emission at 440 nm; with time though, the high amount of sulfur slowly is ripped away from the capping, and the nanoparticles turn into copper sulfide with luminescence emission at 630 nm. The formation of copper sulfide is caused by the presence of an oxide shell of copper and the reaction of this oxide shell with the thiol rich capping moiety. This mechanism allows for producing nanoclusters whose optical properties vary as a function of their composition via sputtering in a controlled atmosphere and a liquid medium. In addition, this shows the importance of the choice of the liquid medium for this technique, as well as the versatility it has.
It was found in the above study that the transformation of copper nanoparticles into copper sulfide occurs over a couple of weeks timespan after sputtering. Therefore we've been developed another method to make the transformation go faster. Considering the way copper sulfide forms, which is mediated by the presence of copper oxide and the conversion of oxide to sulfide, we proposed that the usage of UV-light, irradiated on as-synthesized copper nanocluster dispersions, can provide energy to accelerate the reaction. In this way we obtained photoluminescent copper sulfide nanoclusters in only few hours under UV-light irradiation at room temperature. The reaction speeded up to 20 times compared with a normal formation of copper sulfide by the previously investigated storage method. The results are impressive and contribute a feasible way to produce highly emitting copper sulfide nanoclusters well dispersed in monomers. Furthermore, the finding helps understanding the transformation of copper nanoclusters in rich thiol capping moiety environment obtained via sputtering methods.

The studies presented in this thesis contribute with different approaches to nanoparticles synthesis, for uniform, well dispersed, and highly pure nanoclusters with controlled compositions in liquid via sputtering. The understanding of the formation mechanism of nanocluster in relation to the liquid medium and the sputtering atmosphere is valuable for research in this field.
Key words: Magnetron Sputtering, Photoluminescence Nanoclusters, Titanium Oxide, Copper Nanocluster